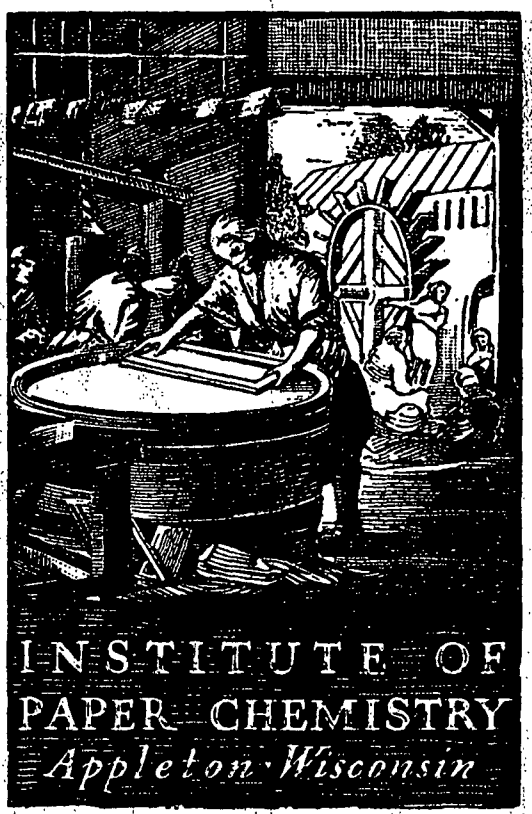

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

Project 2634

Report Five

A Progress Report

to

MEMBERS OF GROUP PROJECT 2634

October 20, 1970

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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MEMBERS OF GROUP PROJECT 2634:

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Bowaters Southern Paper Corporation

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TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

SUMMARY

The Nu Monitor, a completely automatic device for measuring residual lignin in pulp, has been field tested in a bleach plant of Crown Zellerbach Corporation in Camas, Washington. The primary sample was obtained from a 14-in. stock line leading to the chlorination tower. The stock, at 4% consistency, was composed of a mixture of Douglas-fir brown stock, western hemlock brown stock, and colored broke. A completely automatic stock sampling system was designed, constructed, and tested in conjunction with the Nu Monitor.

Field trial results show that the Kappa or permanganate number of the pulp, whichever is desired, correlates within 8.5% of the Nu number as measured by the automated system every seventeen minutes. Through the field trial, redesign data have been obtained that should result in reduction of this error to about 5%. Additional redesign features have resulted from the field trial that will improve component reliability, reduce the overall size of the system, and minimize the amount of service and maintenance required.

Interfacing of the Nu Monitor with an IBM 1800 process control computer was successfully achieved within the limitations imposed by the present design of the Nu Monitor control system.

Negotiations are presently underway with The O'Meara Company, Inc. of Milwaukee, Wis., for the commercial marketing of the system.

INTRODUCTION

This is the final report on the work that was initiated August 1, 1966, with the objective of devising an on-line automatic device for the measurement of residual lignin in pulp.

Initially sponsored by twenty-two pulp and paper manufacturers, this project is now sponsored by fourteen. The first two years of work were devoted to (1) development of a simplified chemical test for lignin and (2) development of an automated method for accurate measurement of the mass of fibers to be tested. The details of the successful development of both will be found in the preceding four reports.

The past two years' work has consisted of the design, construction, and testing of an automatic instrumental system based on the above two developments. Such an instrument has been constructed and tested in the laboratory and in a bleach plant. A means of automatically obtaining a primary pulp sample from a plant process line has also been devised and plant tested.

This report is concerned mainly with the results of the industrial trial of the system in the bleach plant of Crown Zellerbach Corporation, Camas, Washington. The future of the instrument and its commercial availability are also discussed.

PRIMARY PULP SAMPLING SYSTEM

In the bleach plant at Camas, the stock line from which the sample is taken is about fourteen inches o.d. and carries brown stock of about 4% consistency to the chlorination tower. The internal pressure on the line is equivalent to a static head of about thirty feet of water. Figure 1 is a schematic diagram of the sampling system, which is controlled and sequenced automatically by a drum-type programmer and appropriate relays, switches, and timers. All lines prior to the dilution tank are 1 in.

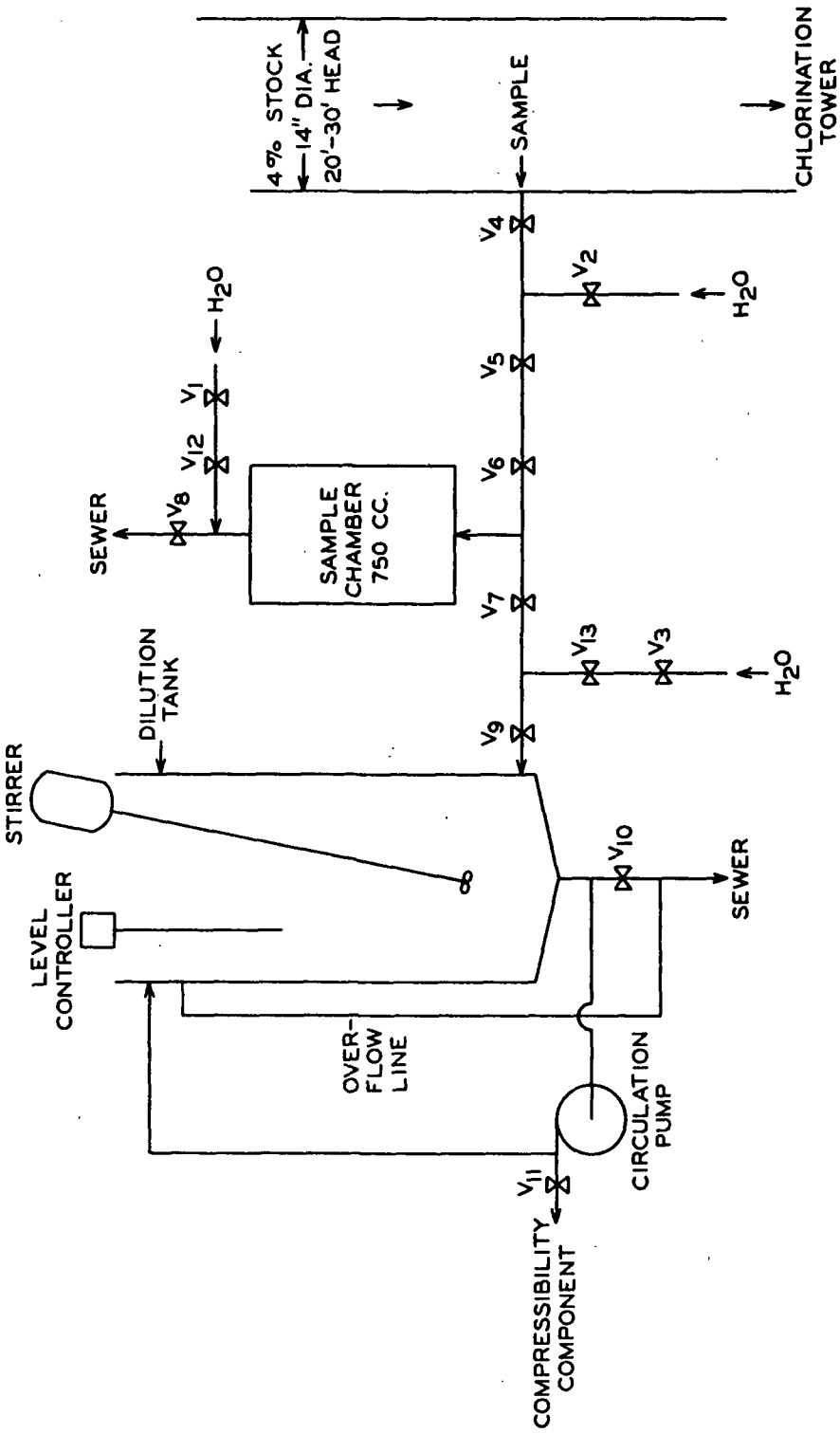
The sampling procedure consists of the following steps, at the beginning of which the circulation pump and stirrer are off and valves V_2, V_6, V_7, V_9, V_{10}, V_{11}, V_{12}, and V_{13} are closed.

- V_6 is opened for twelve seconds, allowing stock to flow from the 14-in. line through the Lucite sample chamber, through V_8, and to the sewer.

- At the end of twelve seconds, the 750 cc. of stock in the sample chamber are transferred to the 20-gal. dilution tank by simultaneously closing V_6 and V_8 and opening V_9, V_7, and V_{12}. Fresh water flowing through V_{12} for twelve seconds washes the pulp into the dilution tank, leaving the sample chamber filled with water.

To bring the sample to 0.2% consistency in the dilution tank, V_{12} and V_7 are closed while opening V_{13}. V_{13} remains open until the tank level reaches the probe of the level controller, and then V_{13} and V_9 are closed simultaneously with the starting of the stirrer and circulation pump.

The sample chamber is flushed with water for five seconds by opening V_{13}, V_7, and V_8. The actual purpose of this flush is to clear the line, leading to the sewer beyond V_8, of pulp which may plug the line if allowed to stand in it.



V_1, V_2, V_3 MANUAL NEEDLE VALVES (STEEL)
V_4 MANUAL GATE VALVE (STEEL)
V_5 MANUAL BALL VALVE (PVC)
V_6, V_7, V_8, V_9, V_{10}, V_{11} PNEUMATIC PLUG VALVES (PVC)
V_{12}, V_{13} SOLENOID VALVES

Figure 1. Stock Sampling System

V_{11} is operated by the control system of the compressibility component as described in Report Four, and allows a fixed volume of the 0.2% stock to flow into this component for testing. The two control systems are interconnected and when the sampling system controller receives a signal that the test sample has been received by the compressibility component, V_{11} being closed again, the pump and stirrer are turned off and V_{10} opens.

When the tank has drained, V_{10} closes and V_9 and V_{13} open to fill the tank with wash water to the level control probe.

V_9 and V_7 close, and the pump and stirrer are operated for 5 seconds.

V_{10} again opens, draining the tank.

V_{10} closes, and V_{13}, V_7, and V_6 open to flush the sample line with water into the 14-in. stock line. This lasts for twelve seconds and prevents plugging of the line with the 4% stock.

The sequence is repeated through Step 4, the prepared sample being held in the dilution tank until called for by the control system of the compressibility component.

The compressibility component (Fig. 24, Report Four) and the dilution tank housed side by side in a steel enclosure five feet high, four feet wide, and two t deep, with the rest of the sampling system in the open between the 14-in. stock and the steel housing. The steel housing is about 2-1/2 feet from the stock .

The complete sample preparation cycle takes less than six minutes, while complete cycle of testing the sample in the compressibility component requires

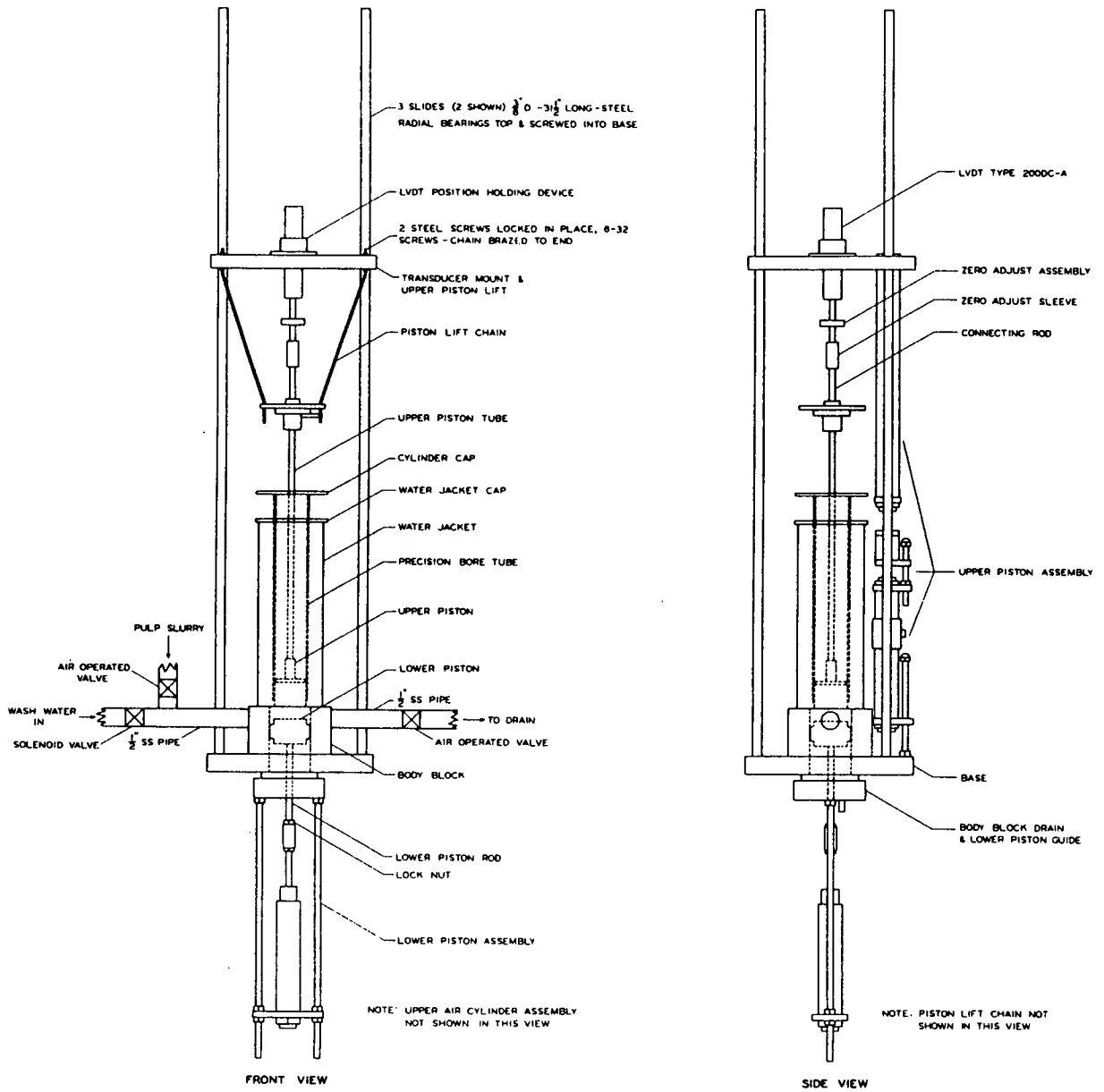


Figure 2. Compressibility Component

7. The upper piston begins a reciprocating motion that lasts for twelve minutes and serves to disintegrate the pad and mix the fibers with the nitric acid.

8. At the end of twelve minutes the upper piston is lowered, again forming a pad of the fibers, and by siphon the nitric acid is drawn off through the hollow upper piston rod, through the flow cell of a split-beam colorimeter where the color intensity of the liquid is measured at 425 nm.

9. The colorimeter output signal, analogous to the light absorbance of the liquid, is read in the same manner as the LVDT.

0. The used sample is flushed from the system, the system itself is flushed with fresh water, and the cycle is repeated.

)LORIMETER

The colorimeter is of the split-beam type where the light beam is split
:ter passing through the flow cell. This is accomplished by a semitransparent
irror set in the path of the beam at a 45° angle to the light path. The reflected
)rtion passes through an optical filter of 425 nm. and then impinges upon the
irface of a photocell. The transmitted portion passes through an optical filter
' 550 nm. and then impinges upon the surface of another photocell. The net
)lorimeter output signal is the difference in the output of the two photocells.
iis design eliminates error due to turbidity or particulate matter in the flow cell
cause the same flux falls upon both photocells.

Figure 3 shows the calibration curve of the colorimeter with a 3-cm. flow
ll in the light path. The relationship between output voltage and light absorb-
ce at 425 nm. was established by passing standard dichromate solutions through the
ow cell. From these data, the regression equation was established by nonlinear

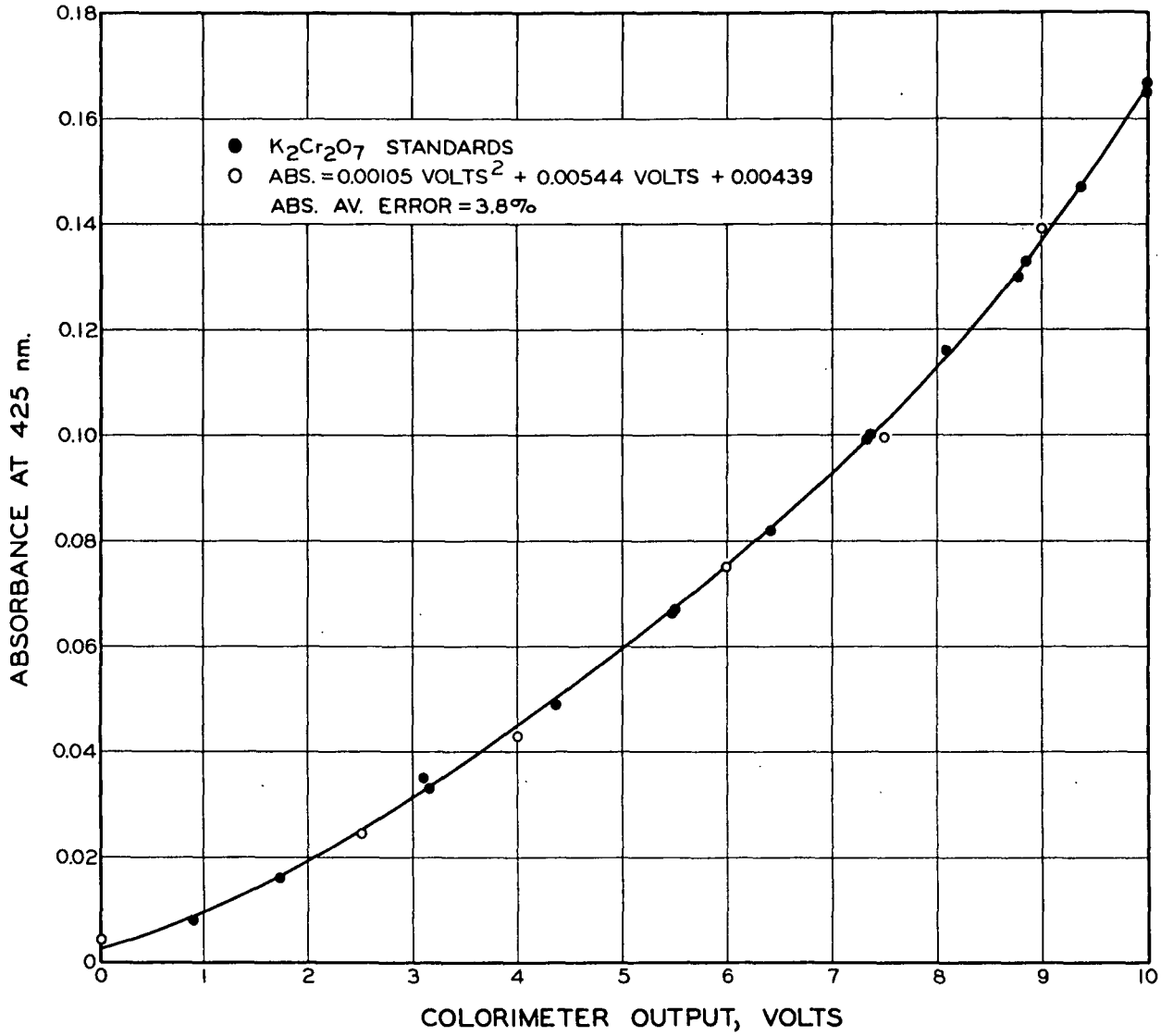


Figure 3. Colorimeter Calibration

regression analysis. The absolute average error is the mean of the residuals expressed as a percentage of the mean experimental absorbance value.

LVDT

A linear displacement transducer (Linear Variable Differential Transformer) mounted at the upper end of the upper piston rod is used to measure the pad thickness (pad weight). This has been described in Report Four. Its calibration curve, pad weight vs. output voltage, is shown in Fig. 4. This curve was established by recording the output voltage after compressing pads of varying thickness for three minutes and then flushing the fibers from the instrument, filtering them off, bringing them to constant weight at 105°C., cooling, and weighing. The regression equation was established from the experimental data. As in past reports, S_{rel} is the standard error of the estimate expressed as a percentage of the mean experimental weight values.

DATA RESULTING FROM AUTOMATIC OPERATION

Data were obtained in two ways: (1) by allowing the system to operate without interference, taking a fresh sample for every 17-minute cycle, and (2) by repetitive measurement of the Nu-value of the 0.2% slurry in the dilution tank. In both cases, sufficient pulp was removed from the dilution tank for subsequent determination of permanganate number, and in some cases, Kappa number. The LVDT and colorimeter readings were recorded manually, and the Nu numbers were subsequently computed from Equation (1) by substitution into it of the absorbance and pad weight values derived from the respective calibration regression equations.

$$Nu = \frac{ABX}{CY} \qquad (1)$$

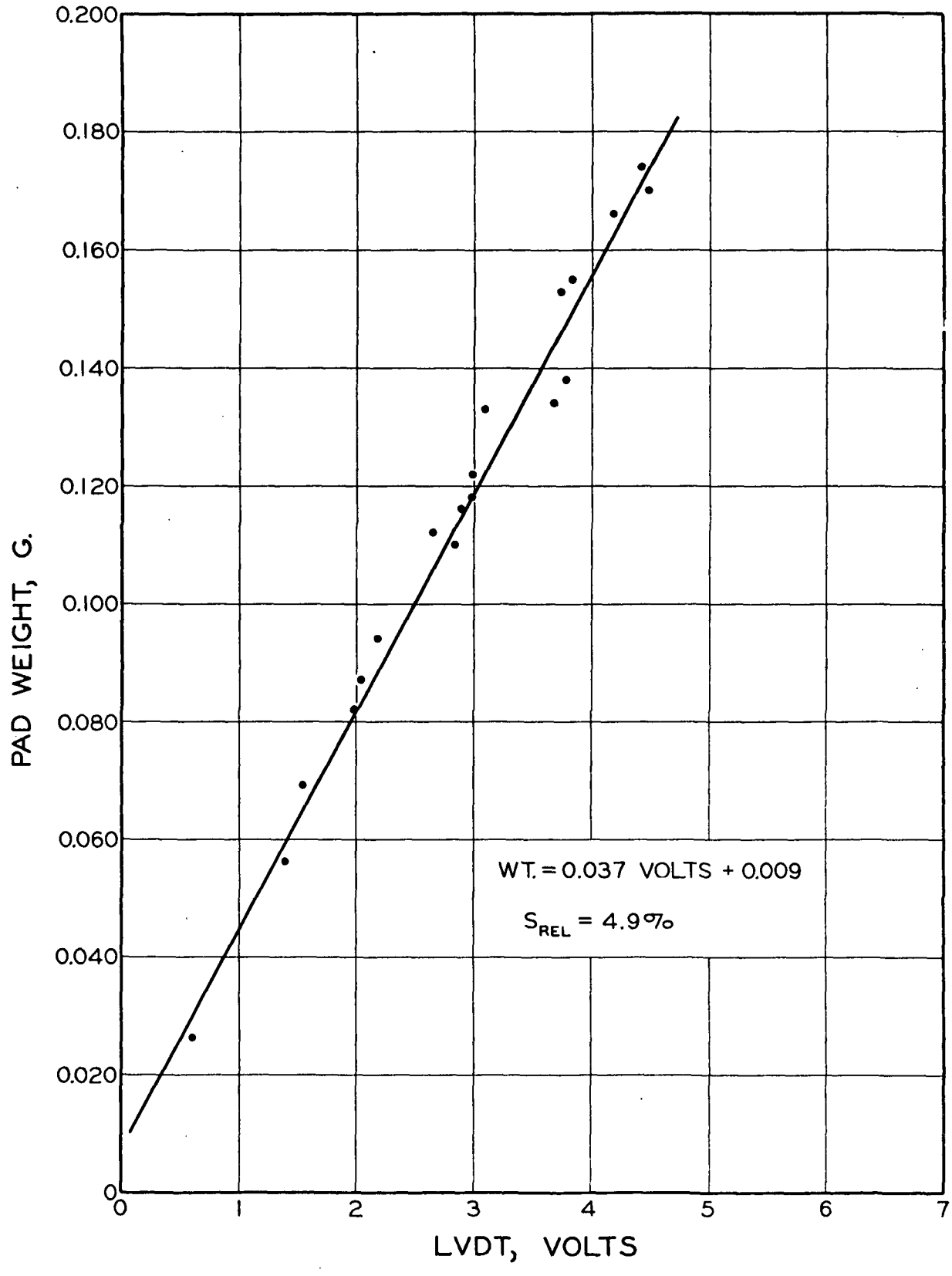


Figure 4. LVDT Calibration

where:

$\underline{A}$ = given $K_2Cr_2O_7$ standard, mg./liter,

$\underline{B}$ = target pad weight, mg.,

$\underline{C}$ = absorbance of $K_2Cr_2O_7$ standard,

$\underline{X}$ = absorbance of reacted HNO_3, and

$\underline{Y}$ = actual pad weight, mg.

Upon making these substitutions, the final equation became:

$$Nu = \frac{6.300V_1^2 + 32.64V_1 + 26.34}{3.682V_2 + 0.896} \qquad (2)$$

where:

$\underline{V_1}$ = colorimeter output voltage, and

$\underline{V_2}$ = LVDT output voltage.

The resulting data are given in Table I. Figure 5 shows the relationship between permanganate number and Nu number, while Fig. 6 shows Kappa number vs. Nu number.

TABLE I

RESULTS OF AUTOMATIC NU MONITOR OPERATION

Sample	Nu	K	Kappa	Sample	Nu	K	Kappa
1a	31.1	21.3		9a	32.9	22.4	
b	31.0			b	30.3		
c	31.1			c	30.8		
d	30.0						
e	29.6			10a	30.5	26.1	
f	28.9			b	30.4		
g	29.7			c	30.8		
2a	28.7	19.9	27.5	11a	29.8	22.2	
b	29.1			b	30.2		
c	28.7			c	28.2		
d	28.5						
e	29.1			12a	29.9	21.5	
f	26.9			b	29.0		
g	28.5			c	29.0		
3a	35.1	22.6		13a	33.8	21.9	
b	31.8			b	32.4		
c	32.1			c	35.6		
d	36.7						
e	36.0			14a	32.7	23.3	
f	35.5			b	31.4		
g	32.6			c	27.1		
4a	28.2	21.2		15a	34.7	27.3	
b	27.9			b	34.1		
c	26.6						
d	27.3			16	34.9	24.6	
				17	33.1	22.7	
5a	26.6	18.8		18	31.1	22.1	
b	22.3			19	31.1	22.4	
c	23.9			20	31.2	22.7	
d	26.0			21	36.3	24.1	
				22	33.3	23.9	
6a	32.6	20.7		23	27.7	18.5	25.2
b	30.3			24	27.0	18.4	25.1
c	31.1			25	25.3	18.1	24.6
d	25.3			26	24.2	17.8	24.6
				27	24.6	17.9	24.7
7a	34.1	21.8		28	26.7	18.0	26.0
b	31.6			29	27.8	18.7	26.1
c	32.6			30	29.4	18.9	26.0
d	32.9			31	28.7	19.2	26.6
				32	29.7	18.7	25.8
8a	34.1	23.6		33	31.2	22.0	30.6
b	32.0			34	31.6	20.9	31.0
c	31.7			35	31.7	22.1	32.9

TABLE I (contd.)

RESULTS OF AUTOMATIC NU MONITOR OPERATION

Sample	Nu	K	Kappa
36	35.1	24.2	35.0
37	36.3	24.2	36.7
38	36.7	23.5	34.4
39	34.3	23.8	33.8
40	27.8	18.6	25.3
41	29.1	18.3	24.7
42	27.2	19.3	25.4
43	23.4	15.6	20.4
44	24.8	14.8	19.3
45	25.1	15.9	21.4
46	31.2	18.7	25.3
47	29.8	17.7	23.8
48	33.7	19.6	28.9
49	38.7	20.5	30.7

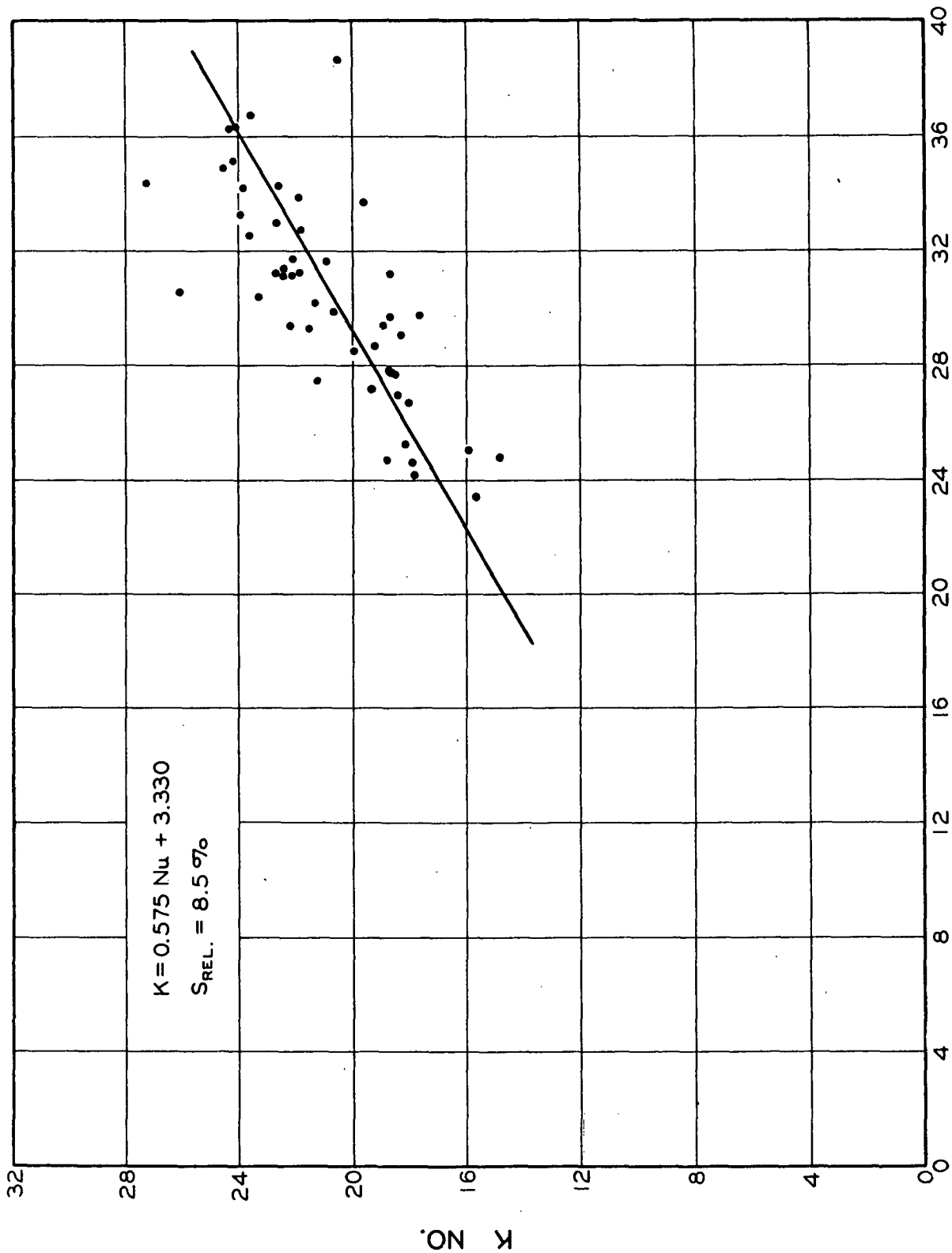


Figure 5. Permanganate Number vs. Nu Number

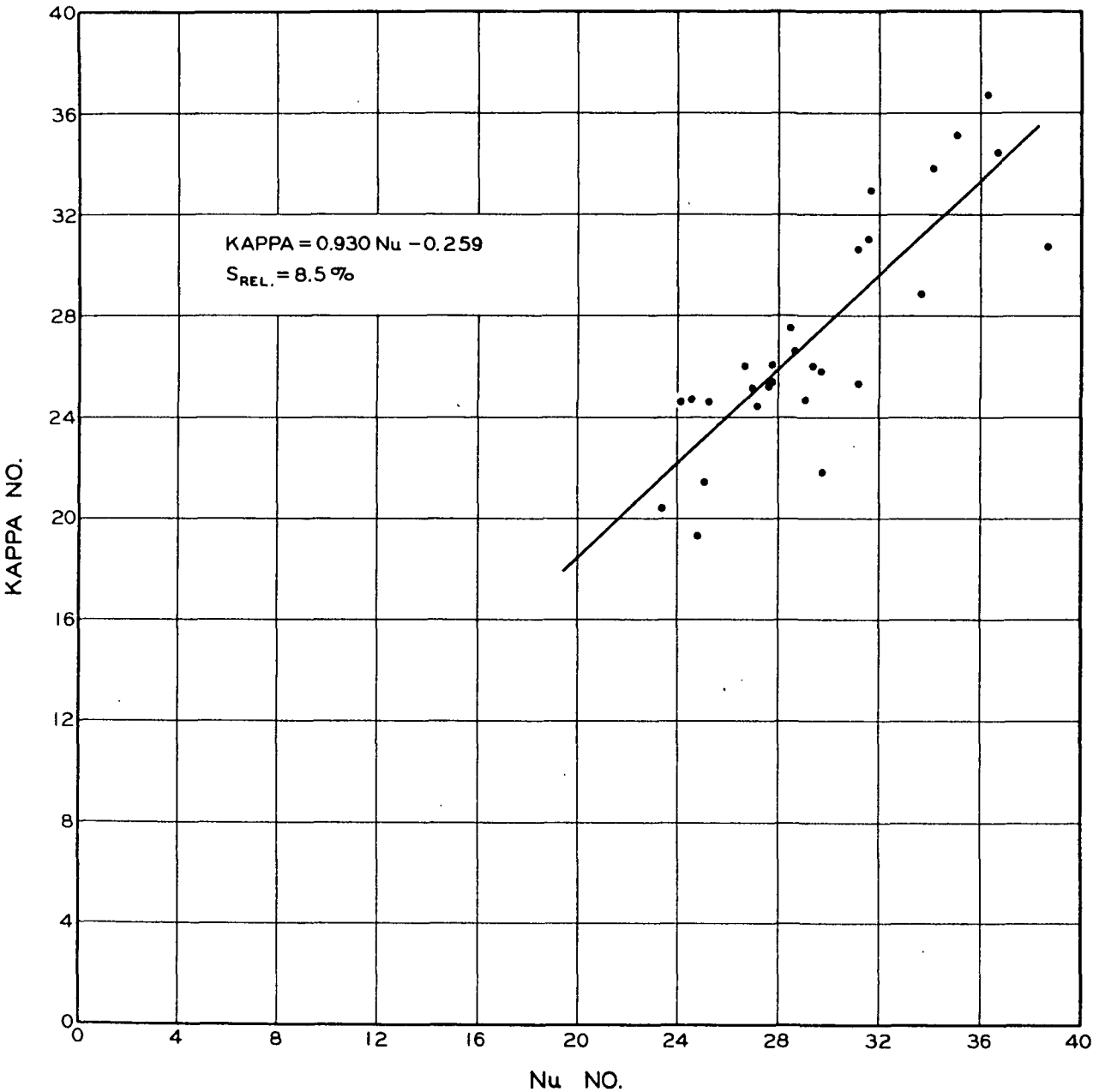


Figure 6. Kappa Number vs. Nu Number

DISCUSSION

SAMPLING SYSTEM

The sampling system shown in Fig. 1 was developed and tested in the laboratory at The Institute of Paper Chemistry, but equipment limitations prevented it from being tested with slurries of greater than 2%. As mentioned previously, the stock to be sampled in the mill was at about 4%. Upon installation of the system in the mill, it was found that the higher consistency stock tended to plug the line between valve V_6 and the 14-in. stock line. For this reason the back-wash system was installed.

After installation of the back-wash system, the plugging problem practically disappeared. Only once did serious plugging occur, and that was after the equipment had sat shut down for a long period of time.

Several of the PVC pneumatic Vanton plug valves failed due to stress at threaded joints in the valve body. This can be prevented in future installations by means of metal reinforcing straps or by specifying metal valve bodies.

COLORIMETER

Operation of the colorimeter has been satisfactory with the exception of a single instance of failure of an amplifier component. This failure required that the amplifier be returned to the manufacturer for repair, and resulted in the loss of two weeks' time in the planned program of testing.

It can be seen from Fig. 3 that the output signal of the colorimeter is not a linear function of the light absorbance of the reacted HNO_3. Actually, the output signal is analogous to light transmittance. In future models of this colorimeter, the user will have the option of specifying either a linear output or an

put similar to that shown in Fig. 3. In those instances where the Nu Monitor is be interfaced with a process control computer, there would be no need for linear- ng the output because of the ease with which the computer can make the simple putations like those of Equation (2).

In those future cases where the Nu Monitor is not to be interfaced with a ge process control computer, the colorimeter output can be linearized for input a small analog device internal to the Nu Monitor. Thus, the Nu Monitor will ld a single output: the Nu number.

T

Unlike previous ones (Reports Three and Four), the calibration curve shown Fig. 4 has a significant positive intercept on the ordinate.

The "zero" reading of the LVDT is established by the same procedure as t by which positive calibration points are established, except that plain water used instead of a fiber slurry. At the end of three minutes' "compression" time, zero adjust assembly (Fig. 3) is moved up or down to yield an output of zero m the LVDT.

From subsequent observation, it is now thought that the high intercept is to fibers in the water filling the precision-bore tube during the zeroing pro- ure. It will be recommended for the future that the LVDT be zeroed only when sh water is placed in the tube by removing the cylinder cap and pouring the water

There is also the possibility of variation in the zero position due to iable seating position of the lower piston. The lower piston seats and seals h a Viton O-ring slightly compressed against the upper portion of the body block.

This variance can be compensated for by the use of a second LVDT to measure the position of the lower piston. The distance between the two piston faces then becomes the difference in the two LVDT outputs, and a more accurate measure of pad thickness (weight) is obtained.

DATA

From Fig. 5 and 6 it can be seen that Kappa and permanganate numbers calculated from the measured Nu number both have a standard error of 8.5%. This seems to indicate that the major portion of the error is due to uncertainty in the Nu number. The sum of the errors in the calibration curves of the colorimeter and LVDT (Fig. 3 and 4) is close to the overall errors in Fig. 4 and 5, thus indicating that the overall error in the Nu number measurement is largely a result of the additive errors in calibration of the colorimeter and LVDT.

Reduction of the LVDT calibration error to about 3% can be accomplished by the methods already discussed. The colorimeter calibration error should be reducible to about 2% by using optical filters instead of liquid solutions. Frequent automatic standardization of both should then maintain the established calibrations. It is doubtful if the overall error of the Nu number measurement can be reduced below about 5% in a commercial instrument.

In Fig. 4 and 5, the Nu values plotted are the mean values of the repetitive measurements and the single determination values when only one measurement was made.

In Table I are shown individual results of the repetitive measurements made on Samples 1 through 15. Table II gives the mean Nu values and the standard deviation, expressed as a percentage of the mean, of the individuals. It can be seen that, in general, replication is quite good.

TABLE II

ANALYSIS OF REPETITIVE NU MEASUREMENTS

Sample	Mean Nu	Standard Deviation, %
1	30.2	2.8
2	28.5	2.4
3	34.3	5.5
4	27.5	2.8
5	24.7	6.9
6	29.8	9.2
7	32.8	2.7
8	32.6	3.3
9	31.3	3.6
10	30.6	0.4
11	29.4	2.9
12	29.3	1.4
13	33.9	3.9
14	30.4	7.9
15	34.4	0.9

MPUTER INTERFACING

Because the two signals (colorimeter and LVDT) from which the Nu number computed are available twelve minutes in time from each other, an intermediate ad-and-hold device was designed and built to store these readings until the M 1800 could read them. The device is shown in Fig. 7. Two such devices were ed, one for the colorimeter and one for the LVDT.

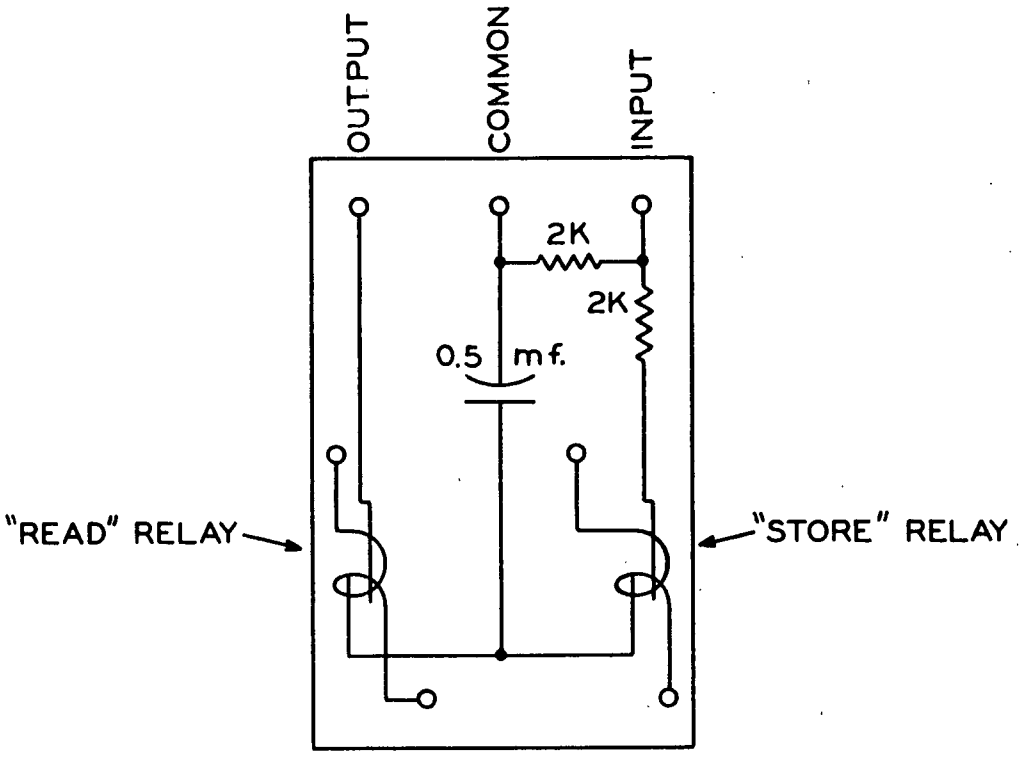


Figure 7. Read-and-Hold Device

The output leads from the LVDT and colorimeter were connected to the ommon and input terminals of the read-and-hold device. Upon the appropriate ommand from the compressibility component control system, the "store" relay ontacts were closed, thus allowing the 0.5-mf. condenser to be charged by the LVDT r colorimeter output voltage. Five seconds were allowed for charging the condenser nd then the relay contacts were opened. After both signals had been stored in heir own read-and-hold devices, the control system sent a low-priority interrupt ignal to the computer.

When the computer acted upon the interrupt signal, an ECO was issued which sulted in the closing of each of the "read" relays. Since the multiplexer inputs re connected to the output and common terminals of the read-and-hold devices rough a bridge circuit to cut the signal to one twentieth of its stored value, e computer was able to read the stored analog signals. Cutting the stored signal one twentieth of its value for input to the computer was required because the ltiplexer was set up only to read signals in the 0 to 500-mv. range, while both DT and colorimeter outputs are in the 0 to 10-v. range. About 1.5 seconds were lowed for reading the stored signals.

Laboratory pretesting of the read-and-hold devices showed that they held e signal for up to fifteen minutes with no detectable loss. However, print-out each signal read by the computer in the mill usually showed a lower value than it read visually from the voltmeters on the Nu Monitor. The difference was metimes as much as 10%.

It was finally discovered that an intermediate relay leading the signal o the read-and-hold device was opening a fraction of a second after the input nal had been cut off, thus allowing a slight discharge of the "hold" condenser.

Use of these intermediate relays in the present system is required because of a shortage of microswitches on the drum programmer. Future models will be designed with sufficient microswitches.

FUTURE

At the present time, negotiations are being conducted between The Institute per Chemistry and The O'Meara Company, Inc. of Milwaukee for the eventual manu- re and marketing of the instrument. It will probably be late summer of 1971 e it is commercially available. Although it is uncertain at this time, the of each unit will probably be around $15,000.

The present unit, being the only one now in existence, is an engineering type, and will be used as the basis for many design changes to be incorporated ture models. The need for these design changes became apparent as the program sting in the mill proceeded. Some of these changes are:

1. automatic standardization of LVDT and colorimeter,
2. location of control systems for both sampling and compressibility component operation in one enclosure,
3. simplification of both control systems,
4. addition of failure indicators,
5. improved reliability of pneumatic valves,
6. use of solid-state plug-in electronic components, where possible, for compactness and ease of maintenance and trouble-shooting.

With these and a number of smaller design changes in the system, mainten- and servicing should be at a minimum. The supply of 15% nitric acid will have replenished occasionally, of course, but a 20-gal. reservoir will last 8-9 of around-the-clock operation.

ACKNOWLEDGMENT

For design and contruction of the read-and-hold devices and for much valuable advice in design of electronic and electric components, the author wishes to thank Mr. Keith Hardacker of the Institute staff.

Dr. John F. Perry, now with Kimberly-Clark Corporation but formerly with the Institute staff, contributed greatly to understanding of interfacing problems and to design of the interfacing system.

Mr. Donald G. Sachs of the Institute staff worked many long hours and contributed greatly to the success of the laboratory and field testing of the Nu Monitor.

The mill trial was made possible through the cooperation of Crown Zellerbach Corporation staff members, especially Messrs. Gary Hollmer, Dudley Church, and Mark Hannah.

THE INSTITUTE OF PAPER CHEMISTRY

Richard B. Kesler

Richard B. Kesler
Research Associate
Division of Materials Engineering
and Processes